Short Course on Molecular Dynamics Simulation

Lecture 5: Boundary Conditions

Professor A. Martini
Purdue University

High Level Course Outline

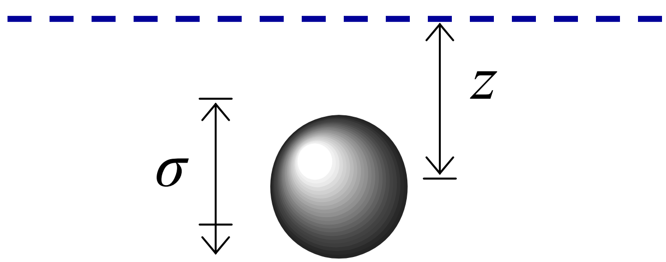
1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD

Boundary Conditions & Minimum Images

- Fixed simulation cell boundaries
  - Repulsive boundary
  - Atomistic rigid walls
  - Atomistic semi-rigid walls
    - Massive boundary atoms
    - Spring potential
- Periodic boundary conditions
- Minimum image criteria

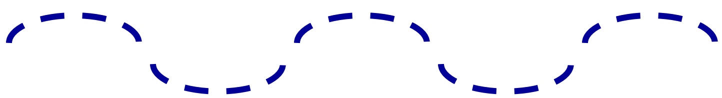
Fixed Boundaries

- Continuous barrier potential
  - Simplest case, flat repulsive boundary



$$u(z) = \varepsilon \left(\frac{z}{\sigma} \right)^{-12}$$

  - Virtual barrier texture introduced through more complex expressions such as the (10-4-3) potential

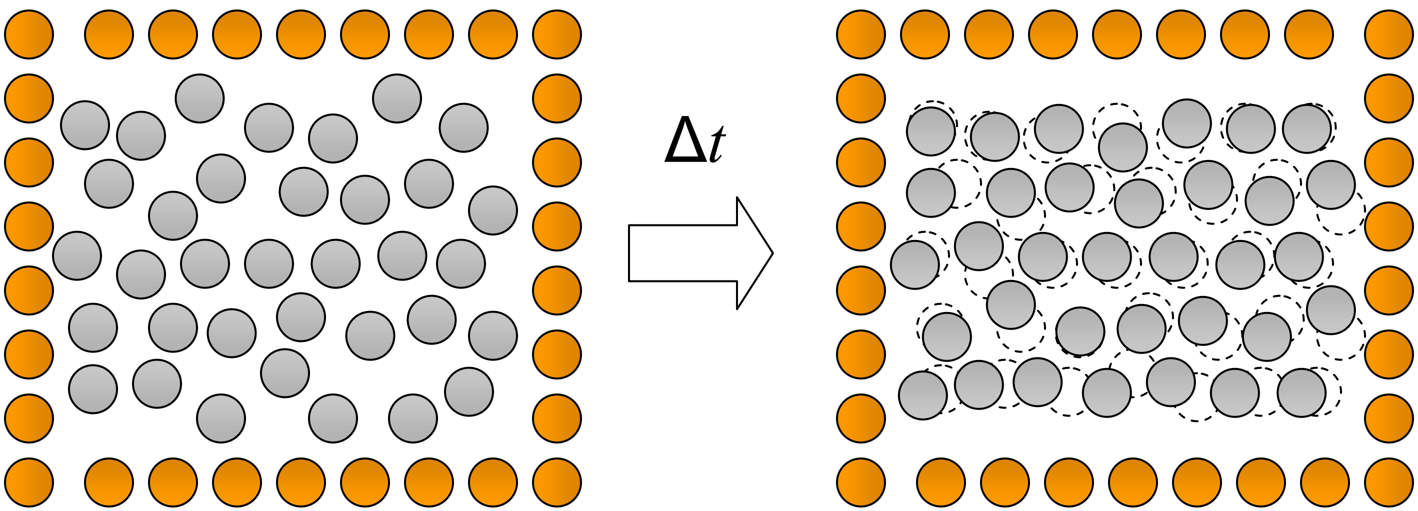


Continuous function representing the (100) face of an fcc lattice ⇒

$$u(z) = 2\pi \left[\frac{2}{5z^{10}} - \frac{1}{z^4} - \frac{1}{3/\sqrt{2}\left(z + 0.61/\sqrt{2}\right)^3} \right]$$

Fixed Boundaries

- Rigid atomistic walls

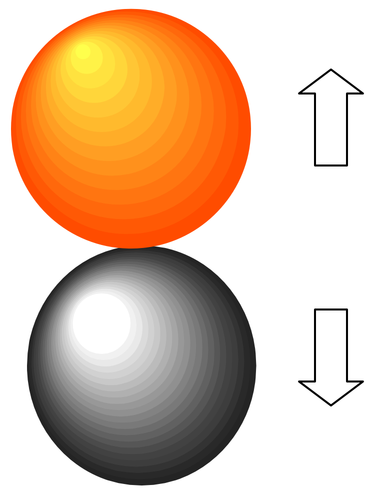


Fixed Boundaries

- Semi-rigid atomistic boundary → massive boundary atoms
  - Massive boundary atoms will be affected less by inter-atomic interactions
  - Consider the interaction between a boundary and a non-boundary atom where

$$m_b >> m$$

m_b



$F \rightarrow a_b = F/m_b$

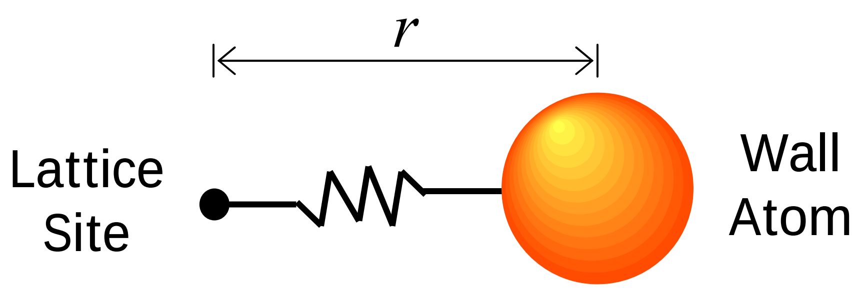
$F \rightarrow a = F/m$

m

$$a_b << a$$

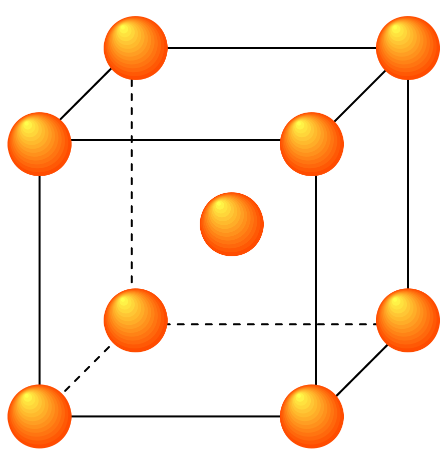
Fixed Boundaries

- Semi-rigid atomistic boundary → spring potential
  - Boundaries both rigid enough to maintain structure and flexible enough to interact with the other atoms

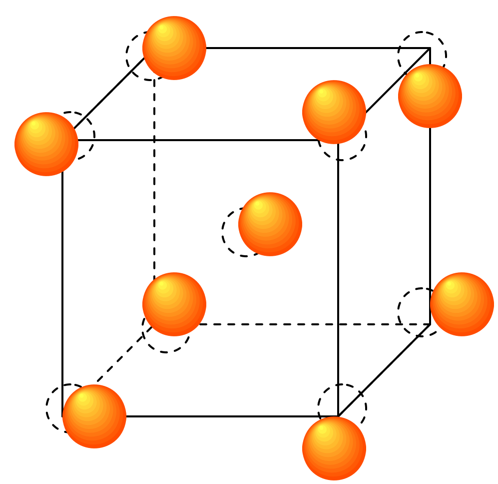


$$u(r)=\frac{1}{2}k\left(r-r_{lattice}\right)^2$$

Initial bcc configuration:

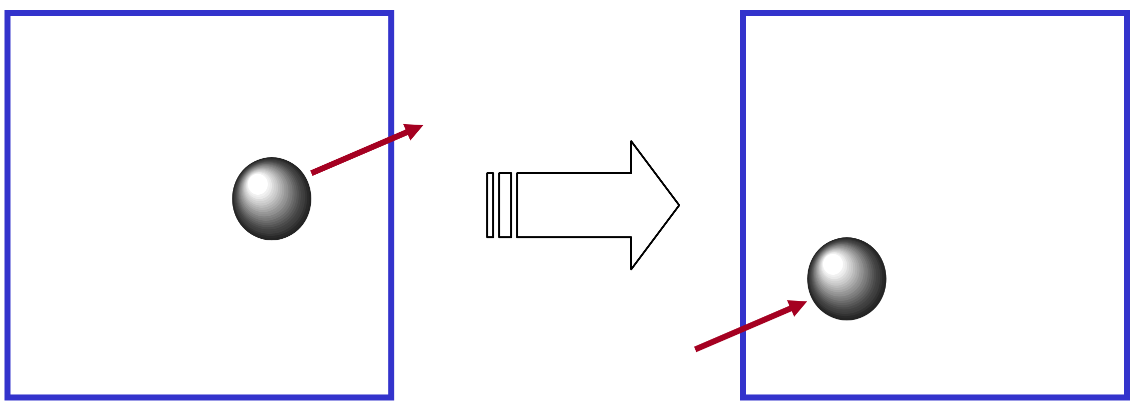


During MD simulation:



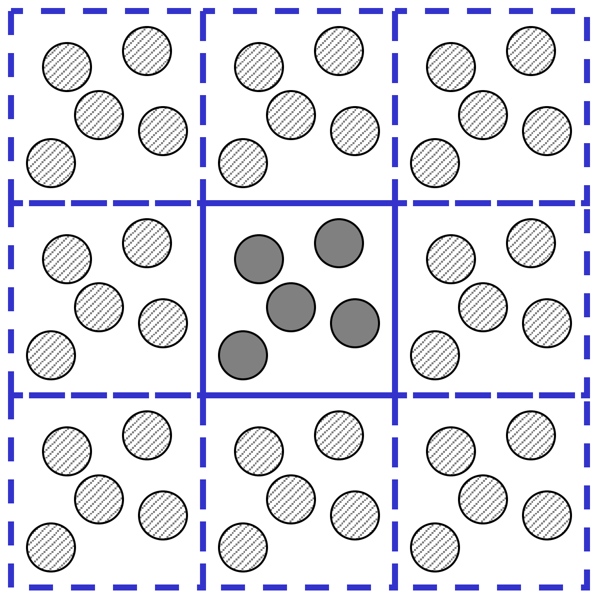
Periodic Boundary Conditions

- PBCs enable macroscopic properties to be calculated from fewer particles
- Simulated interactions of “bulk” material
- Out one side, in the other



Periodic Boundary Conditions

- The primary cell is replicated in all simulated direction as image cells
- Primary and image cells have the same
  - Number, position, momentum of atoms
  - Size
  - Shape

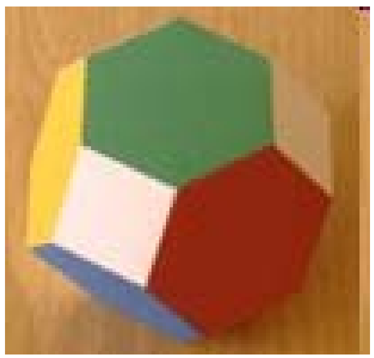


Periodic Boundary Conditions

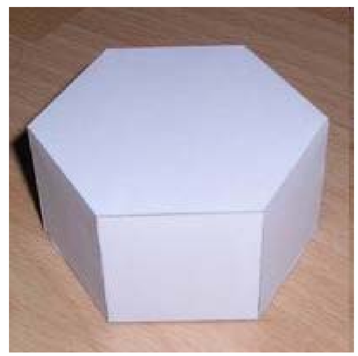
- The shape of a periodic simulation cell must fill all space by translational operations of the central box in 3D

Cube

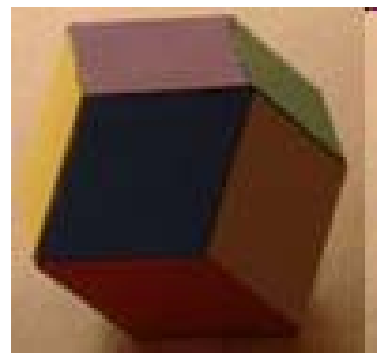
Truncated Octahedron



Hexagonal Prism

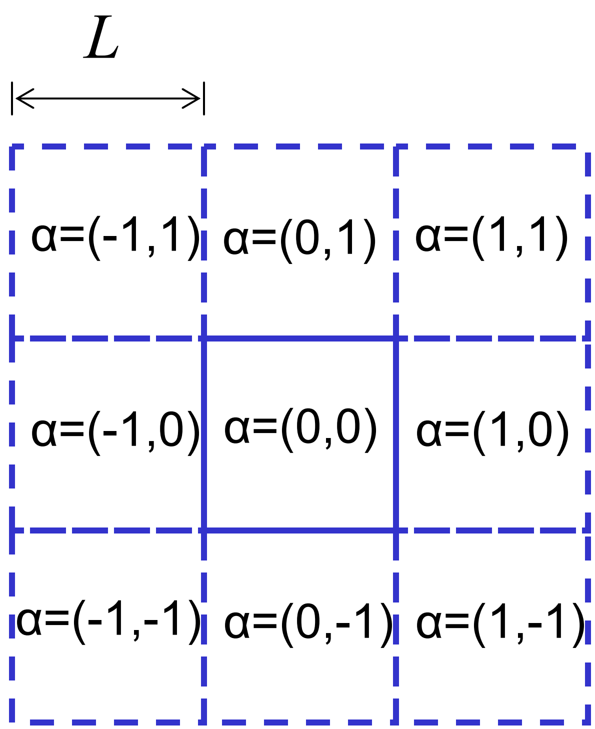


Rhombic Dodecahedron



Periodic Boundary Conditions

- Forces between primary and image atoms



If i and j are in the primary cell:

$$\vec{F}_i = -\frac{\partial U(\vec{r}_{ij})}{\partial \vec{r}_i}$$

If j is in an image cell:

$$\vec{F}_i = -\sum_{\vec{\alpha}} \frac{\partial U(\vec{r}_{ij} - \vec{\alpha} L)}{\partial \vec{r}_i}$$

Periodic Boundary Conditions

$$\vec{F}_i = -\sum_{\alpha_x=-1}^{+1}\sum_{\alpha_y=-1}^{+1}\sum_{\alpha_z=-1}^{+1}\frac{\partial U(\vec{r}_{ij}-\vec{\alpha}L)}{\partial \vec{r}_i}$$

- Minimum image distance
  - Atom i can experience a force from atom j and its 26 images
  - But only one image is a distance less than ½L
  - So if the pair potential is truncated at $r_c \leq 1/2\ L$, either atom j or only one of its images can exert force on atom i
  - With PBCs, interactions are truncated *at least* to this minimum image distance